Calibration of the Mossbauer Isomer Shift of 119Sn

I. 6 Calibration of the Mössbauer Isomer Shift of ^{119}Sn

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The isomer shift (δ) is one of the most important quantities which can be measured by Mössbauer spectroscopy, giving a unique information about the environment of the Mössbauer atom, e.g., the chemical valence state of the atom. This quantity is expressed as a product of a nuclear quantity and an atomic one;

$$\delta = \frac{4\pi}{5} Ze^2R^2 \left(\frac{\Delta R}{R}\right) \cdot \Delta|\psi(0)|^2 , \qquad (1)$$

where $\Delta R/R$ is the relative difference of the nuclear radius between the excited and the ground states, and $\Delta|\psi(0)|^2$ is the difference of electron density for different atomic environments. Knowledge of $\Delta R/R$, therefore, can help interpret δ in terms of electron density related with atomic environment; thus $\Delta R/R$ plays as the calibration of Mössbauer isomer shift δ. To determine the value of $\Delta R/R$ it is necessary to determine $\Delta|\psi(0)|^2$, and in the case of the 23.87 keV Mössbauer transition of ^{119}Sn, the latter have been estimated from the changes of i) internal conversion of valence electrons[1], ii) nuclear life time of the 23.87 keV level[2], and iii) NMR Knight shift.[3] The internal conversion method is of course the most direct way in obtaining $\Delta|\psi(0)|^2$, at least for ^{119}Sn, since in this case the change of total electron density can be attributed to that of valence electron density;

$$\Delta|\psi(0)|^2 = \Delta|\psi_{5s}(0)|^2 . \qquad (2)$$

In the present work we re-determine $\Delta R/R$ of the 23.87 keV transition of ^{119}Sn by the conversion method[1], taking advantage of the CYRIC cyclotron, the Mössbauer spectrometer and the EMIS of Tohoku University, together with the iron-free β-ray spectrometer of IPCR (Inst. Phys. Chem. Res.).

The 23.87 keV transition of ^{119}Sn was fed from the EC decay of ^{119}Sb to ^{119}Sn; ^{119}Sb was obtained by a milking method from ^{119m}Te which was produced by irradiating a natural Sb target with a 38 MeV proton beam from the CYRIC cyclotron. The radioactive ^{119}Sb was implanted into various materials using the EMIS (Electro-Magnetic Isotope Separator) at an acceleration voltage of 20 kV. The implantation dose rate was $\lesssim 10^7$ atoms$\cdot$cm^{-2}s^{-1} for the mass number of 119, and the implanted number of ^{119}Sb was $\lesssim 10^{12}$ atoms$\cdot$cm^{-2}, which was measured with a LEPS. In order to identify the chemical state of the implanted ^{119}Sb and to determine δ, emission Mössbauer spectra were measured at T = 77 K and 150 K

using a standard absorber of $CaSnO_3$. Mössbauer spectra of ^{119}Sb implanted into white tin and $CaSnO_3$ taken at T = 77 K are shown in fig. 1.

Conversion electron spectra of the same samples that were used in Mössbauer spectroscopy were measured with the iron-free β-ray spectrometer at IPCR. A momentum resolution of 0.14 % was achieved. The detector was a gas-flow proportional counter having a thin window (~ 100 $\mu g/cm^2$ polypropylene). All the conversion lines of the 23.87 keV transition were measured. In fig. 2 are shown the conversion spectra in the region of N and O lines. Since in the N-O region K-LM Auger lines are present we also measured the Auger spectrum using a ^{117m}Sn source produced by the $^{116}Cd(\alpha,3n)$ reaction at CYRIC and IPCR in order to subtract the Auger contribution. The relative conversion intensity ratios O/N_I were evaluated using the computer code ACSEMP.[4)]

In fig. 1 the Mössbauer spectrum of white tin shows a single line indicating a unique implantation site, but the spectrum of $CaSnO_3$ indicates composite site; the line A corresponds to the normal substitutional site in $CaSnO_3$ but the line B should correspond to an environment similar to that of white tin because of the similar isomer shifts. In correlating conversion intensity to isomer shift in the case of composite site one must know the site population, which we obtained from the temperature dependence of Mössbauer spectrum (T=77K and 150 K) as P_A = 47 % and P_B = 53 % for the present sample of implanted $CaSnO_3$. Thus we could subtract the contribution of site B from the conversion spectrum of $CaSnO_3$, assuming that the conversion intensity of site B is equal to that of white tin (Sn) from the equality of δ, and obtained

$$(O/N_I) = \begin{cases} 0.120 \pm 0.015 & \text{for Sn ,} \\ 0.066 \pm 0.013 & \text{for } CaSnO_3 \text{ (A) .} \end{cases} \tag{3}$$

From these values we obtained the valence electron density using the formula ($O_I \leftrightarrow 5s$, $N_I \leftrightarrow 4s$)

$$|\psi_{5s}(0)|^2_{exp} = |\psi_{4s}(0)|_{theor} \cdot (O/N_I)_{exp} , \tag{4}$$

and assuming eq. (2), and thus deduced the electron-density difference between white tin (Sn) and $CaSnO_3$;

$$\Delta|\psi(0)|^2 = |\psi_{5s}(0)|^2_{CaSnO_3} - |\psi_{5s}(0)|^2_{Sn} = -38 \text{ a.u.,} \tag{5}$$

where we used the relativistic value of Band et al.[5)] for the theoretical 4s density $|\psi_{4s}(0)|^2_{theor}$ = 719 a.u. in eq. (4). It is noted that in eq. (4) O shell is identified as O_I, i.e., the $O_{II,III}$ conversion is neglected relative to the O_I conversion. Finally we obtain ΔR/R from the measured δ and eq. (1) as

$$\Delta R/R = +1.2 \times 10^{-4} , \tag{6}$$

where the plus sign indicates that the 23.87 keV state has a larger nuclear radius than the ground state.

Experiments using other implantation substrate materials are also in progress.

References

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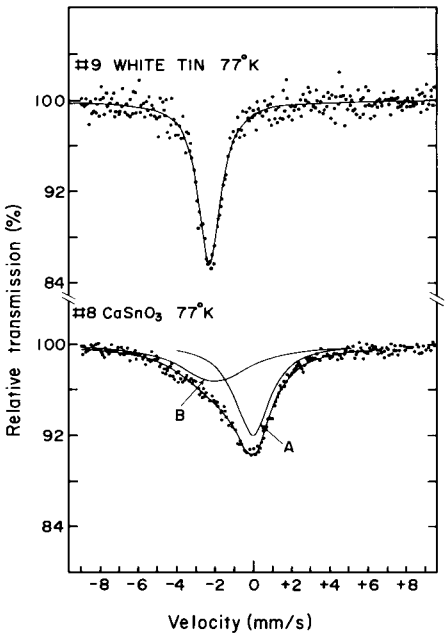

Fig. 1. Mössbauer spectra of ^{119}Sb implanted into white tin and $CaSnO_3$. The spectra were measured at T = 77 K using a standard absorber of $CaSnO_3$ at the same temperature. For ^{119}Sb in $CaSnO_3$ (No. 8 sample) there are two implantation sites A and B; for interpretation see the text.

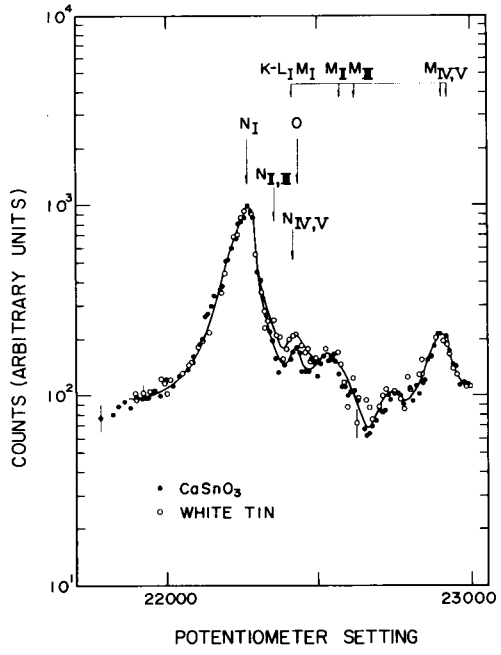

Fig. 2. Conversion electron spectra of the same samples that were used in Mössbauer measurement; filled circles correspond to ^{119}Sb in $CaSnO_3$ and blank circles to ^{119}Sb in white tin. The spectra are normalized at N_I line. Note the overlapping $K\text{-}L_IM_I$ Auger line.